

PROCESS DEVELOPMENT FOR BIOMASS LIQUEFACTION

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INTRODUCTION

The U.S. Department of Energy's Biomass Liquefaction Experimental Facility at Albany, Oregon, was constructed for the purpose of developing biomass to oil conversion processes. Facility equipment was sized to process 1-3 tons per day of wood chip equivalent. Process development work has been underway at Albany since the summer of 1977. A multitude of reactant and product handling difficulties have resulted in numerous facility and process modifications. Presently, there are two main versions of the CO-Steam process being tested at Albany. The original process, called the Bureau of Mines Process (BOM) because it was developed by researchers at the former Bureau of Mines facility near Pittsburgh, involves dried and ground wood chips slurried in a heavy oil medium. The newer process is called the LBL process, since it was developed by staff members of the Lawrence Berkeley Laboratory. In the LBL process wood chips are broken down into a pumpable water slurry by acid hydrolysis. In either process the slurry is then pumped into a high temperature, high pressure reactor wherein the biomass oil is formed through the action of carbon monoxide and steam under the influence of a sodium carbonate catalyst. The role of the Pacific Northwest Laboratory (PNL) in the process development effort has been twofold, 1) provide bench scale process development experimental support and 2) provide analytical support as needed. The bench scale work has involved for the most part batch autoclave tests and this work has been reported elsewhere.^(1,2,3) This paper provides the details of the latest analytical work completed on the biomass derived oil.

PROCESS DESCRIPTIONS

BOM Process -

The Albany facility was originally constructed to develop the process of biomass conversion to fuel oil in a recycling oil slurry mode. As shown diagrammatically in Figure 1. Wood chips are dried, ground and mixed with oil at 20-30% solids to provide a pumpable slurry. Anthracene oil, a coal tar distillate is used as the start-up slurry oil. This slurry along with carbon monoxide and aqueous sodium carbonate are pumped at high pressure 2000-4000 psig through a scraped-surface preheater and into a stirred tank reactor. The average residence time in the reactor can be varied from 20 to 90 minutes at temperatures ranging from 300°C to 370°C. After leaving the reactor the product is cooled and the pressure is let down into a flash tank where fixed gases and most of the water is removed. A major change in the original process flow is the replacement of the centrifuge in the product cleanup stage with a vacuum still. After pressure let down the product is reheated and flashed in the still where a light product oil is drawn off; a middle fraction is recovered and a portion is recycled for slurry makeup; and heavy product, solids and catalyst residue are removed from the still bottom. This is the extent of the unit operations at Albany, however, the total process plan would have the still bottoms pumped to a gasifier for production of CO/H₂ gas feed for the liquefaction process. Sodium could be leached from the gasifier ash and could be recycled to the process probably after reaction with carbon dioxide from the offgas and gasifier product gas.

LBL Process -

There are several basic differences between this process and that for which the Albany facility was designed. However, through plumbing modifications the plant was made to operate in this mode, and, in fact, the first large scale wood oil production was by this process. By the LBL process (Figure 2) the wood chips are reduced directly to a pumpable aqueous slurry through an acid hydrolysis step without preliminary drying and grinding. By this hydrolysis step the wood to water ratio can be maintained at a level equivalent to the wood to oil ratio used in the BOM process. The aqueous slurry must then be made basic by sodium carbonate addition and then passes through the plant in the same manner as in the BOM process. After pressure letdown a gravity separation is made of oil from water and the product can then be distilled as a clean-up step. No recycle oil is used in the LBL process as it is essentially a once through process for the biomass. The aqueous stream will likely have to be recycled to recover the catalyst residues and other soluble organics.

PRODUCT ANALYSIS

After approximately 15 months of operation of the Albany facility in various configurations by the BOM process, no pure (or nearly pure) wood derived oil had yet been produced. This was due to various mechanical difficulties. The major difficulty was the inability to remove residual solids from the product stream because the product clean-up centrifuge would not operate effectively in this process. The build-up of residual materials in the system led to increases in viscosity over time and the eventual plugging and shut down of the test run before the start-up oil could be effectively purged from the system. The initiation of LBL process tests at Albany in the spring of 1979 led to the first production of nearly pure wood oil in May and the first large scale production of catalytically converted wood oil in September of 1979. This oil is the basis for the analytical work reported here. Due to the differences in the processes, primarily the acid hydrolysis step, it is likely that there will be some differences between the LBL process oil described here and that produced by the BOM process. It has been suggested, based on the amount of degradation of the wood, that the major effect of the hydrolysis is to break down the hemicellulose with minor effect on the cellulose and little or no effect on the lignin portion of the wood.

Vacuum Distillation Procedure -

A vacuum fractional distillation of wood oil was performed by the use of an ASTM-D1160 distillation apparatus with a modified receiver which allows fraction collection while continuing the distillation under vacuum. The fractions collected are described in Table 1. Fraction #1 includes both the water which was dissolved or emulsified in the wood oil as well as a light oil fraction which was immiscible with water and distilled in the same temperature range. The codistillation could be the result of similar boiling points or may also be the result of a steam distillation phenomenon. The atmospheric true boiling points were calculated based on the instructions included in the D1160 procedure. The distillation was discontinued at the point that decomposition of the product in the still pot became evident. The decomposition point is approximately 100°F below that experienced for petroleum crude oils.

Analysis of Distillate Fractions -

A summary of the analytical data derived from the wood oil and its distillate fractions is presented in Table 2. The elemental analyses show a trend of increasing carbon content from the lighter to heavier fraction and a stronger reverse trend in hydrogen content. The hydrogen to carbon atomic ratio as a result shows a trend from nearly 2 in the lightest fraction to less than 1 in the still bottoms.

TABLE 1. Vacuum Fractional Distillation of Wood Oil
ASTM-D1160 For Sample TR7-136

Fraction	Actual Amount	Relative Amount	Color	TBP atm	TBP 10mm
#1	8 ml Light Oil 23 ml Water	3% 8%	Clear	To 280°F	To 50°F
#2	45 ml	18%	Clear To Yellow	280-510°F	50-270°F
#3	35 ml	14%	Green To Orange	510-600°F	270-330°F
#4	40 ml	16%	Orange	600-720°F	330-470°F
#5	20 g	8%	Orange To Brown	720-810°F	470-510°F
Residue	86.6 g	32%	Dark Brown	Above 810°F	Above 510°F (Pot at 630°F Decomposition)

TABLE 2. Analytical Data for Distillation Fractions

Fraction	C	H	N	O	Atomic H/C	Hc	C ¹³ NMR Ali/Aro C	H ¹ NMR Ali/Aro H
#1 (Oil Layer)	78.8	12.0	0.0	9.7	1.31	16,000	12	30
#2	77.2	9.9	0.0	13.3	1.52	15,200	1.1	10.0
#3	77.1	8.9	0.0	13.4	1.37	15,100	1.0	7.3
#4	79.2	8.9	0.5	12.1	1.33	15,800	1.2	6.6
#5	79.4	7.9	0.2	12.3	1.19	15,100	1.0	5.3
Residue	82.3	6.5	0.0	10.4	0.94	14,900	---	---
TR7-136 (Including 8% Water)	72.3	8.6	0.2	17.6	1.41	14,500	0.53	---

The oxygen content is less patterned in that it is lowest in the light distillate, maintains a higher nearly constant level through most of the distillate range then drops to a lower level in the still bottoms. This data is mirrored in the heats of combustion results for the various oils. It is interesting to note that the nitrogen appears for the most part in two of the heavier distillate fractions but not in the still bottoms. Elemental sulfur analysis puts the content at 0.006% for the total wood oil; (4) similar analyses for the distillate fractions were not performed.

The use of proton and C¹³ nuclear magnetic resonance spectrometry (NMR) and infrared spectrophotometry has provided some insights into the chemical structure of the wood oil components. The C¹³ NMR data shows a fairly even balance between saturated and unsaturated carbon in the distillate oils. However, proton NMR shows a much larger amount of aliphatic hydrogen in proportion to aromatic hydrogen. There is essentially no olefinic hydrogen. Aromatic compounds, as a result of molecular bonding and structure have a lower hydrogen to carbon ratio than aliphatics, (one

or less for aromatic, greater than 2 for aliphatic). The disproportionately large amount of aliphatic hydrogen is an indication of the large amount of aliphatic substitution on the aromatic ring structures. This data is an average of dozens of chemical compounds and as such shows a trend of decreasing amounts of aliphatic compounds and of aliphatic substitution on the aromatic rings through the distillation range. The proton NMR data also show the presence of other functional groups such as furans in fraction #2 and naphthalenic and aromatic acid and ester compounds in fractions #4 and #5. The methoxy aromatic structure is very prominent in fraction #2 but is also evident in the heavier fractions. Long chain oxygen containing alkyl groups disappear from prominence after fraction #2, however, the ethyl ether functional group remains prominent throughout. The infrared spectra of these fractions do not provide nearly so definitive results as the NMR spectra, however, they generally confirm the above-stated conclusions.

We have thus far been able to identify a significant number of the actual components of the distillate fractions of the wood oil through the use of Gas Chromatography Mass Spectrometry (GCMS). The components in Table 3 were identified by analysis of computer matched data. Those compounds listed with a question mark could not be matched due to the limitations of the computer search library, but were determined by analysis of the mass spectra. In addition, the acid functional groups shown in fraction 4 and fraction 5 were identified in derivatized (trimethylsilylation) samples of the wood oil fractions. Work continues in this area as those compounds identified are not nearly all the compounds present, and no quantification of this analysis has yet been done.

TABLE 3. Chemical Components of Wood Oil Fractions by GCMS

<u>Fraction #1</u>	<u>Fraction #2</u>	<u>Fraction #3</u>
C ₆ Diene	Methyl Pentenal	Propyl Guaiacol
Methyl Cyclopentene	Formyl Dihydropyran	Dimethyl Methoxy Phenol?
(Two Isomers)	Dimethyl Furan	Trimethyl Methoxy Phenol?
Methyl Hexadiene	(Two Isomers)	C ₄ Methoxy Phenol?
2-Pentanone	Trimethyl Furan	C ₇ Phenol?
Dimethyl Hexadiene	Guaiacol	C ₈ Phenol?
2-Methyl Cyclopentanone	Furfural	Dimethyl Naphthol
Methyl Cyclopentadiene	Ethylstyrene	Trimethyl Naphthol
Ethyl Benzene	Para Cresol	
Cyclo Octane	4-Methoxy Phenol	<u>Fraction #4</u>
Dimethyl Heptene	Methyl Indan	Methyl Naphthol
C ₃ Benzene	Dimethyl Phenol	(Two Isomers)
Indan	Ethyl Phenol	Dimethyl Naphthol
Guaiacol	Dimethyl Indan	(Seven Isomers)
Furfural	Methyl Ethyl Phenol	Trimethyl Naphthol
Methyl Indan	(Two Isomers)	Alkylated Hydroxy Phenyl Acids?
(Three Isomers)	Trimethyl Phenol	(MW 138-206)
Dimethyl Indan	Dimethyl Ethyl Phenol	<u>Fraction #5</u>
(Five Isomers)	Dihydroxy Acetophenone	Alkylated Hydroxy Phenyl Acids?
Ethyl Styrene	Sec Butyl Phenol	(MW 182-224)
	Propyl Guaiacol	

Additional analytical results from petroleum crude oil test methods have also been produced for the wood oil.⁽⁴⁾ These tests, performed at Southern Petroleum Laboratories, Inc., are indicative of the difference between LBL process wood-derived oil and crude petroleum. The numbers in Table 4 show that the wood oil is a heavy non-aliphatic oil. The high solids and salt content will likely be reduced to nearly zero by the vacuum distillation step of product clean-up. Neutralization numbers for the distillable fractions of the oil ranged from 17.7 to 5.3 when expressed in units

of mg KOH/gr. The existant gum ranged from 621 to 827 mg/100 ml sample of the same distillable fractions.

TABLE 4. Analysis of LBL Process Wood-derived Oil

API Gravity @ 60°F	-4.93
Specific Gravity @ 60°F	1.12
Density @ 60°F lbs/gal	9.31
Pentane Soluble, Volume Percent	3.25
Salt, lbs/1000 bbls	79.4
Total Solids, BS&W	8.0

From Reference 4

ECONOMIC ANALYSIS

An economic evaluation of the two processes under study at Albany was performed and the results presented earlier this year.⁽⁵⁾ This study was undertaken with very little continuous pilot scale data available and as such provides only a rough estimate of the projected economics. It does indicate that with the present technology the product oil will be expensive. Table 5 is a summary of the relevant data.

TABLE 5. Cost Data for Wood-derived Oil

	LBL Process	BOM Process
Capital Cost		
2000 Green ton/day	\$39.5 million	\$56.1 Million
Product Cost		
\$/Million BTU	\$ 7.98	\$ 8.56
100% equity		
\$/Million BTU	\$ 6.59	\$ 6.82
65/35 debt/equity		
\$/barrel	\$45.7	\$42.7
100% equity		
\$/barrel	\$37.8	\$34.0
65/35 debt/equity		
Mid 1979 constant dollars		
15% DCF ROR on equity		
Debt interest rate 9% long term, 10% short term		
Wood cost at 1.25/million BTU (\$11/green ton)		

From Reference 5

These calculations are for a commercial sized plant including many unit operations which have not yet been demonstrated at the Albany scale of operation and as such are based to a significant degree on engineering judgment. The conclusion from the economic analysis was that the processes appear to be viable technically and that significant cost reductions may be possible through process improvement and optimization. There are many remaining questions relative to the Albany processes. Process development work at DOE's Experimental Facility should provide answers to these questions. These answers will likely have a significant effect on process costs, however, it is not entirely clear whether the costs will increase or decrease. An additional area which will require analysis will be the use of the wood oil as a petroleum substitute in chemical production. The separation and use of various chemical fractions of the wood oil is presently under study at PNL.

CONCLUSIONS

When considered for use as a substitute fuel oil, wood oil as produced at Albany by the LBL process appears qualitatively to fall somewhere between petroleum derived #6 Fuel Oil and the synthetic oil derived from the Occidental Flash Pyrolysis process as shown in Table 6. Wood oil falls nearly half way between the other two oils in nearly all categories except that wood oil is very low in sulfur content.

TABLE 6. Comparison of Some Fuel Oils

	C	H	N	O	S	Ash	Moisture	H _c BTU/lb	Density g/ml
Wood Oil	72.3	8.6	0.2	17.6	0.006	.078	3.5	14500	1.19
Dry Wood Oil (by calculation)	80.2	8.5	0.2	11.1	0.006	.085	0.0	15800	--
#6 Fuel Oil	85.7	10.5	2.0	0-3.5	0-3.5*	0.05	0.20	13200	1.02
Pyrolytic Oil	57.0	7.7	1.1	33.2	0.2	0.5	14	10600	1.39

* Legal sulfur limit determined by use site, e.g., 0.35% maximum in Los Angeles County

This comparison is valid on a chemical basis, however, as stated earlier the use of wood oil purely as a substitute fuel is not currently economically attractive. Despite the large amount of resources already expended on research of this process, it remains in a developmental stage and new technology could have a significant impact on the process economics. The alternate use of wood oil as a chemical feed-stock is also being studied.

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REFERENCES

1. Elliott, D.C. and Walkup, P.C., "Bench Scale Research in Thermochemical Conversion of Biomass to Liquids in Support of the Albany, Oregon, Experimental Facility", Presented at the Thermochemical Conversion Systems Coordination Meeting at Ballston Spa, NY, 26 October 1977 (TID 28415).
2. Elliott, D.C. and Giacoletto, G.M., "Bench Scale Research in Biomass Liquefaction in Support of the Albany, Oregon, Experimental Facility", 3rd Annual Biomass Energy Systems Conference Proceedings, 5-7 June, 1979, SERI, Golden, Colorado, pp 123-130, SERI/TP-33-285.
3. Elliott, D.C., "Bench Scale Research in Biomass Liquefaction by the CO-Steam Process", presented at the 29th Canadian Chemical Engineering Conference at Sarnia, Ontario, Canada, 30 September-3 October 1979.
4. Winfrey, J.C., "A Laboratory Evaluation of Biomass Oil (TR7-136)", prepared for Rust Engineering by Southern Petroleum Laboratories Inc., Lab Report #77782, December 1979.
5. Kam, A.Y., "Hydrocarbon Liquids and Heavy Oil from Biomass: Technology and Economics", IGT Symposium Energy from Biomass and Wastes IV, 21-25 January 1980, Lake Buena Vista, Florida.

FIGURE 1

BOM PROCESS DIAGRAM

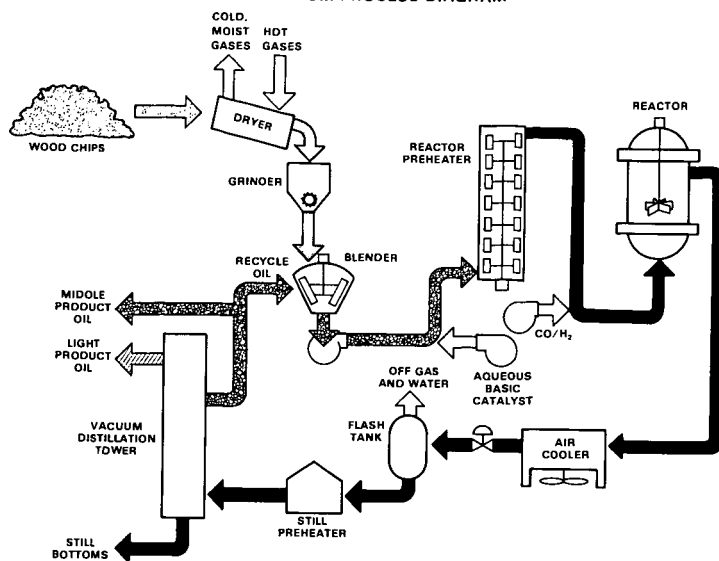


FIGURE 2

LBL PROCESS DIAGRAM

